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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a requ st for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53 (c).

Express Mail Label No.

INVENTOR(S)

Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
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☐ *Additional inventors are being named on the _____ separately numbered sheets attached hereto*

TITLE OF THE INVENTION (500 characters max)

FIRE-RETARDANT COMPOSITE MATERIAL

CORRESPONDENCE ADDRESS

Direct all correspondence to:

☒ Customer Number 22919 *Type Customer Number here* → *Place Customer Number Bar Code Label here*

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ENCLOSED APPLICATION PARTS ***(check all that apply)***

☒ Specification *Number of Pages* 18 ☐ CD(s), Number

☒ Drawing(s) *Number of Sheets* 2 ☒ Other (specify) Petition for Foreign Filing License

☒ Application Data Sheet. See 37 CFR 1.76

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT

☐ Applicant claims small entity status. See 37 CFR 1.27.

☒ A check or money order is enclosed to cover the filing fees

☒ The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: 50-1836

FILING FEE AMOUNT ($) 290

☐ Payment by credit card. Form PTO-2038 is attached.

The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

☒ No.

☐ Yes, the name of the U.S. Government agency and the Government contract number are: _____.

Respectfully submitted,
SIGNATURE [signature]

Date Dec. 17.2003

TYPED or PRINTED NAME Kiyoe K. Kabashima

REGISTRATION NO. (*if appropriate*) 54,874

TELEPHONE 202-293-0444

Docket Number: DK-US035133

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C., 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C. 20231.

DK-US035133

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	:	
	:	ATTN.: Office of Licensing and Review
Shinji MURAKAMI et al.	:	
	:	
For: FIRE-RETARDANT COMPOSITE MATERIAL	:	EXPEDITED HANDLING REQUESTED
	:	

PETITION FOR LICENSE FOR FILING FOREIGN APPLICATION UNDER 35 U.S.C. § 184 AND 37 C.F.R. § 5.13

Assistant Commissioner of Patents
Washington, DC 20231

Sir:

Petitioners, Shinji Murakami and his employer, DAI-ACT, 20 Olympic Drive Orangeburg, NY 10962, respectfully request on an expedited basis, a foreign filing license be granted to file foreign applications pursuant to 35 U.S.C. § 184 and 37 C.F.R. § 5.13 pertaining to the subject matter disclosed in the attached document (Provisional application). A duplicate of this Petition is attached pursuant to 37 C.F.R. § 5.13. The subject matter of the attached document is filed concurrently as a Provisional patent application in the U.S. Patent and Trademark Office.

Petitioners respectfully request the Office of Licensing and Review to telephone the undersigned to confirm that a foreign filing license has been granted. Please direct all telephone calls and all written correspondence in connection with this license to the undersigned.

The Commissioner is hereby authorized to charge the petition fee of $130.00 under 37 C.F.R. § 1.17(h) and any other fees which may become due with respect to this communication to Deposit Account No.: **50-1836**.

12/19/2003 HGUTEMA1 00000021 60529987
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Respectfully submitted,

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Fire-Retardant Composite Material

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention generally relates to a fire retardant composite material. More specifically, the present invention relates to a composite material imparted with a fire spread retardation ability by providing a fluoropolymer layer therein, and also relates to a process of manufacturing such fire retardant composite material.

Background Information

[0002] Conventionally, composite materials are used to manufacture panels and parts for transit vehicles and ships to reduce the weight of such transit vehicles and ships. Although composite materials are superior in terms of weight reduction compared with metal structures, it is inferior to metal materials such as steel sheets in terms of the ability to retard the spread of a fire. Therefore, there are a number of fire safety standards for composite materials to assure their fire resistance. In the United States, the transportation industry requires manufacturers of composite materials to have their products comply with National Fire Protection Association standard #130 in order to delay the spread of a fire and reduce smoke generation at the time of a fire.

[0003] Many of such composite materials use glass fibers as one of the components. Although glass fiber itself is noncombustible, it does not function as a fire retardant when used in a composite material. Therefore, composite materials made of glass fiber and matrix resin cannot comply with the standard. Furthermore, in case of large-sized composite materials, foams, engineered panels like honeycomb, or prepared wood like balsa are used as core materials to reduce cost and weight and to provide insulation and other physical properties. In that case, the surface layers of the composite materials must be structured with higher resistance to fire.

[0004] Conventionally, fire-retardant composite materials have, for instance, a surface coating layer (gel coat) provided as a surface layer to provide aesthetic and other properties, and can be made to reduce smoke generation during a fire. Conventional fire spread retardant composite materials may also have ignition-delaying materials positioned in between the surface layer and the glass fiber layer/core layer, which is molded into the structure of the composite. Generally, it has been known that ignition can be delayed and the fire spread can be retarded by using as a thermal insulation layer a hydrate powder

combined with the matrix resin. Such thermal insulation layer allows water to be evaporated when the temperature elevates, thus slowing the spread of a fire along the surface of the composite.

[0005] Figure 1 shows an example of conventional composite materials used for vehicles.

[0006] The composite material has a basic sandwich structure having a balsa core member 12 and two glass fiber layers 11A and 11B. As fire retardant layers, the composite includes an intumescent mineral wool based fire layer 13, similar to Technofire®, a product of Technical Fibre Products Ltd., and aluminum tri-hydrate (ATH) 14, a glass matt (formed from glass fibers) 15, a gel coating 16 which is a surface coating layer, and a matrix resin that is impregnated to laminate these layers. Each layer is impregnated with the matrix resin, so that, upon curing, the layers are attached to one another to produce the composite material. The ATH powder 14 can be blended into a matrix resin and used to bond the glass mat 15 to the surface coating 16. However, since ATH-blended matrix resins are higher in viscosity and tend not to spread uniformly when applied to the layers, it is difficult to obtain a uniform layer of fire protection in composite material made by this process.

[0007] It has also been also conceived to use a sheet of PTFE (polytetrafluoroethylene) as a fire retardant layer, instead of using an ATH-blended matrix resin. In such cases, it has been conceived to attach a sheet of PTFE onto layers of glass fiber. However, such PTFE sheet does not adhere to the glass fiber layer well, and tends to come off easily due to the expansion of resin at high temperature and the difference of thermal expansion between the PTFE layer and the glass fiber layers.

[0008] In view of the above, it will be apparent to those skilled in the art from this disclosure that there exists a need for an improved fire-retardant composite material that overcomes the problems described above. This invention addresses this need in the art as well as other needs, which will become apparent to those skilled in the art from this disclosure.

SUMMARY OF THE INVENTION

[0009] An object of the invention is to provide a composite material having a porous fluoropolymer layer, which can be readily impregnated with the matrix resin and possesses an ability to retard the spread of a fire.

[0010] The present invention in its first aspect provides a fire retardant composite material having a fire retardant layer having a porous fluoropolymer layer, a structural layer, and a matrix resin impregnated at least partially into the porous fluoropolymer layer and the structural layer such that the porous fluoropolymer layer and the structural layer are attached to one another. In this composite material, a fire spread retardation ability is imparted to a composite material by using a porous fluoride resin layer as a fire retardant layer, so that even when the surface of the composite material is burned, the porous fluoropolymer layer slows the spreading of the fire along the exposure surface. Furthermore, the thickness of the composite material can be advantageously reduced in comparison with a conventional fire retardant layer that has ATH and intumescent, char creating insulation layers.

[0011] The present invention in its second aspect provides the fire-retardant composite material of the first aspect, where the porous fluoropolymer layer is made of at least one selected from the group consisting of expanded PTFE, woven fabric, non-woven fabric, felt, fiber, and powder.

[0012] The present invention in its third aspect provides the fire-retardant composite material of the first or the second aspect, where the porous fluoropolymer layer is made of non-melt-processable resin.

[0013] The present invention in its fourth aspect provides the fire-retardant composite material of any one of the first through third aspects, where the porous fluoropolymer layer is made of PTFE. Here, a PTFE resin is used to manufacture the porous fluoropolymer layer material of the composite. PTFE exhibits the highest LOI (limiting oxygen index) value of 95. Besides, since PTFE has a high melting viscosity, the composite can be imparted with excellent dimensional stability at high temperature, while providing an excellent ability to retard the spread of a fire.

[0014] The present invention in its fifth aspect provides the fire retardant composite material of any one of the first through fourth aspects, where the fluoropolymer resin layer is made of PTFE fabric. Here, the use of a PTFE fiber (fiber diameter from 1 μm to 200 μm) for a porous material advantageously increases the degree of resin impregnation. Due to the greater resin impregnation of such porous material compared with a porous drawn membrane, the time required for impregnation process can be reduced. The fluoropolymer fabric allows for better bond strength to surrounding reinforcement material and gel coat

as the matrix resin can penetrate through the fabric more easily and completely than with an expanded membrane made of other forms of PTFE. Thus, a layer of fluoropolymer fabric helps to prevent blistering and de-lamination even better.

[0015] The present invention in its sixth aspect provides the fire-retardant composite material of any one of the first through third aspects, where the porous fluoropolymer layer is made of modified PTFE.

[0016] The present invention in its seventh aspect provides the fire-retardant composite material of any one of the first through third and sixth aspect, where the modified PTFE is created by copolymerizing PTFE with at least one selected from the group consisting of hexafluoro propene, chloro trifluoro ethylene, perfluoro(alkyl vinyl ether), perfluoro(alcoxy vinyl ether), trifluoro ethylene, perfluoro alkyl ethylene, vinylidene fluoride, and ethylene.

[0017] The present invention in its eighth aspect provides the fire-retardant composite material of any one of the first through seventh aspects, where the porous fluoropolymer layer has a mean CP porous diameter of at least 0.5 μm.

[0018] The present invention in its ninth aspect provides the fire-retardant composite material of any one of the first through eighth aspects, where the porous fluoropolymer layer has a mean CP porous diameter of at least 4.5 μm.

[0019] The present invention in its tenth aspect provides the fire-retardant composite material of any one of the first through ninth aspects, where the matrix resin is at least one selected from the group consisting of vinyl ester resin, vinyl ester bromide resin, epoxy resin, unsaturated polyester resin, epoxy acrylate resin, polyimide resin, phenolic, and bismaleimide resin.

[0020] The present invention in its eleventh aspect provides the fire retardant composite material of any one of the first through tenth aspects, where the structural layer is made of at least one selected from the group consisting of glass fiber, carbon fiber, alumina fiber, silicon carbide fiber, boron fiber, p-Aramid fiber, polybenzimidazol fiber, poly-ether-ether keton (PEEK), graphite, and poly-p-phenylbenz-bisthiazol fiber.

[0021] The present invention in its twelfth aspect provides the fire-retardant composite material of any one of the first through eleventh aspects, where the structural layer includes first and second reinforcement layers and a core layer. The core layer is provided between the first and second reinforcement layers, such that one of the porous

fluoropolymer layer and the core layer is provided at a surface of one of the first and second reinforcement layers, and the other of the porous fluoropolymer layer and the core layer is provided at a surface of the other of the first and second reinforcement layers.

[0022] The present invention in its thirteenth aspect provides the fire-retardant composite material of the twelfth aspect, where the porous fluoropolymer layer is combined with one of said first and second reinforcement layers by entanglement in advance.

[0023] Here, wrinkling and deformation of a PTFE fiber that tends to occur at the time of filling the mold prior to resin impregnation can be prevented by combining the PTFE fiber and the structural layer by entanglement or blending. This way, the amount of resin filled between the structural layer and the fluoropolymer resin layer can also be reduced. This interlamination of the structural layer and the fluoropolymer layer can reduce construction time and manufacturing bottlenecks by unifying multiple processing steps. Furthermore, de-lamination of the fluoropolymer layer due to the expansion of the matrix resin at high temperature and the difference of thermal expansion between the two fiber layers can be prevented.

[0024] The present invention in its fourteenth aspect provides the fire-retardant composite material of any one of the first through twelfth aspects, where fire retardant layer further includes an intumescent layer that is interposed between the porous fluoropolymer layer and the structural layer.

[0025] The present invention in its fifteenth aspect provides the fire-retardant composite material of the fourteenth aspect, where the fire retardant layer further includes a holding layer that is interposed between the intumescent layer and the fluoropolymer layer to hold the intumescent layer to the structural layer.

[0026] The present invention in its sixteenth aspect provides the fire-retardant composite material of the fifteenth aspect, where the porous fluoropolymer layer is combined with the holding layer by entanglement or blending in advance.

[0027] The present invention in its seventeenth aspect provides the fire-retardant composite material of any one of the first through sixteenth aspects, where at least one of the porous fluoropolymer layer and the structural layer has one of hydroxide, salt, and oxide of an alkali-earth metal mixed therein. Here, an alkali earth is mixed within the porous fluoropolymer layer or in close proximity thereto. This way, fluoride that is

generated at time of pyrolysis of the PTFE layer can be neutralized. For instance, premixing calcium with the porous fluoropolymer layer induces a reaction to neutralize hydrofluoric acid, thereby yielding calcium fluoride and preventing generation of hydrogen fluoride, which is a toxic gas, at the time of fire.

[0028] The present invention in its eighteenth aspect provides the fire-retardant composite material of any one of the first through seventeenth aspects, further including a surfacing coating layer applied over the fire retardant layer.

[0029] The present invention in its nineteenth aspect provides a method of manufacturing a fire-retardant composite material, having steps of a surface coat to an inner surface of a mold to form a surface coat layer; forming a porous fluoropolymer layer over the surface coat layer; placing a sheet of structural layer onto the fluoropolymer layer; placing a core member onto the structural layer; impregnating matrix resin at least partially into the core member and the structural layer, such that the structural layer is attached to the core member; and impregnating matrix resin at least partially into the structural layer and the porous fluoropolymer layer, such that the porous fluoropolymer layer is attached to the sheet of structural layer.

[0030] These and other objects, features, aspects and advantages of the present invention will become apparent to those skilled in the art from the following detailed description, which, taken in conjunction with the annexed drawings, discloses a preferred embodiment of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0031] Referring now to the attached drawings which form a part of this original disclosure:

[0032] Figure 1 is a schematic diagram of a conventional composite material having a fire-retardant layer;

[0033] Figure 2 is a schematic diagram of a composite material in accordance with a first embodiment of the present invention;

[0034] Figure 3 is a schematic diagram of a composite material in accordance with a second embodiment of the present invention; and

[0035] Figure 4 is a schematic diagram showing one of the methods of manufacturing a composite material in accordance with the second embodiment of the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0036] Selected embodiments of the present invention will now be explained with reference to the drawings. It will be apparent to those skilled in the art from this disclosure that the following descriptions of the embodiments of the present invention are provided for illustration only and not for the purpose of limiting the invention as defined by the appended claims and their equivalents.

[0037] <Fire-retardant composite material>

[0038] Referring initially to Figure 2, a composite material is illustrated in accordance with a first embodiment of the present invention. The composite material has a basic structure which includes a porous fluoropolymer fiber layer 23 and a glass fiber layer 21. These layers 23 and 21 are impregnated with a matrix resin, such that these layers 23 and 21 are attached to one another.

[0039] Referring next to Figure 3, a composite material is illustrated in accordance with a second embodiment of the present invention.

[0040] The composite material includes a structural layer, a fire retardant layer, a surface coating layer, and a matrix resin. The structural layer includes a balsa core layer 32, which is the thickest layer, and first and second glass fiber layers (reinforcement layers) 31A and 31B. The fire retardant layer is provided over the second glass fiber layer 31B and includes a porous fluoropolymer fiber layer 33, a glass veil layer 36 (an example of the holding layer), and an intumescent layer 37. The intumescent layer 37 is disposed adjacent to the second glass fiber layer 31B. The glass veil layer 36 is interposed between the porous fluoropolymer fiber layer 33 and the intumescent layer 37. The surface coating layer is a gel coat layer 35, which is provided over the porous fluoropolymer fiber layer 33.

[0041] The matrix resin laminates and bonds the layers 31-37 to produce the composite material. The matrix resin is either hand-laid or infused in the layers 31-37 to attach the layers 31-37 to one another by impregnation.

[0042] In this embodiment, the porous fluoropolymer fiber layer 33 includes calcium mixed therein. This is to neutralize fluoride generated at time of pyrolysis of the porous fluoropolymer fiber layer 33, and to yield calcium fluoride

[0043] In general, the thickness of each layer is 0.5 to 2 mm for each of the glass fiber layers 31A and 31B, 4 to 18 mm for the core layer (balsa) 32, 0.1 to 1 mm for the PTFE fiber fire-retardant layer 33, and 1 mm for the gel coating layer 35, respectively. Therefore, the fire retardant layer of the present invention measures about 2 mm, much

thinner than that of a conventional fire retardant layer, which is about 3-5 mm. In addition, to further improve the ability to retard the spread of a fire, the layer of intumescent, char forming material 37 and the glass veil layer 36 are provided in between the surface layer 35 and the second glass fiber layer 31B. The intumescent layer 37 is made of an intumescent mineral wool material such as Technofire®, a product of Technical Fibre Products Ltd. Such intumescent layers generally expand when exposed to heat, and create an insulation layer of char to slow the spread of fire. Once the intumescent layer becomes a layer of char, it becomes weak and tends to fall off when subjected to vibration or shock. The glass veil layer 36 is provided to prevent the intumescent layer 37 from falling off and hold the intumescent layer 37 to the glass fiber layer 31B. In order to allow the intumescent layer 37 to expand, the glass veil layer 36 is preferably made of a non-woven glass fiber.

[0044] Although the glass fiber layers are used as the reinforcement layers 31A and 31B in this embodiment, these reinforcement layers 31A and 31B may be made of any one of woven glass fiber, carbon fiber, alumina fiber, silicon carbide fiber, boron fiber, p-Aramid fiber, polybenzimidazol (PBI) fiber, poly-ether-ether keton (PEEK), graphite, and poly-p-phenylbenz-bisthiazol (PBO) fiber. Similarly, although non-woven glass fiber is used as the holding layer 36 in this embodiment, the holding layer 36 may also be made of any one of the materials listed above.

[0045] The matrix resin may be any resin selected from the group consisting of vinyl ester resin, vinyl ester bromide resin, epoxy resin, unsaturated polyester resin, epoxy acrylate resin, polyimide resin, phenolic, and bismaleimide (BMI) resin. To attain an improved ability to retard the spread of a fire, refractory material, vinyl ester bromide may be used as the matrix resin.

[0046] Alternatively, instead of using separate layers, the porous fluoropolymer layer 33 and the glass fiber layer 36 may be combined into one layer in advance prior to the assembly of the composite material. Such combination can be accomplished by, for example, using physical blending of the fibers and densifying the two layers together, or entanglement by using needle punch or water jet needle punch. In this case, in addition to improved workability, the use of pre-interlaminated layers decreases a gap between the glass veil layer 36 and the porous fluoropolymer layer 33. In this manner, the ability to

retard the spread of a fire at the interface between the glass veil layer 36 and the porous fluoropolymer layer 33is further improved.

[0047] <Porous fluoropolymer layer>

[0048] The porous fluoropolymer layer 33 is formed on the second glass fiber layer 31B, over the glass veil layer 36 and the intumescent layer 37, by attaching a porous fluoropolymer film made of any material selected from non-melt-processable resins such as PTFE and modified PTFE, and melt-processable resins such as ETFE (ethylene-tetrafluoroethylene copolymer) and PCTFE (polychlorotrifluoroethylene) among others. The porous fluoropolymer layer 33 is most preferably made of PTFE in this embodiment. PTFE is the most preferable because of its high melt viscosity. Due to its high melt viscosity, the PTFE layer is not likely to drip when it is molten. Accordingly, it is possible to prevent the spread of a fire that is caused by dripping melt-processable resin.

[0049] In this embodiment, the porous fluoropolymer layer 33 is made of non-woven fiber with a fiber diameter of 1 μm to 200 μm. Alternatively, the porous fluoropolymer layer 33 can be in the form of expanded PTFE, woven fabric, felt, fiber, or powder. Woven fabric is generally made by weaving yarns or filaments. Non-woven fabrics are generally made by mechanical blending of the fibers, or by melt processing. Since it is apparent to one ordinarily skilled in the art how to manufacture porous material from expanded PTFE, woven fabric, non-woven fabric, felt, fiber or powder, further explanation and illustration will be omitted herein.

[0050] Non-melt-processable resins, PTFE and modified PTFE:

[0051] The porous fluoropolymer layer can be made from a non-melt-processable resin. Such non-melt-processable resins include, for example, PTFE and modified PTFE. PTFE generally has a viscosity of 10^{11} poise. Modified PTFE is created by copolymerizing PTFE with modification agents such as hexafluoro propene, chloro trifluoro ethylene, perfluoro(alkyl vinyl ether), perfluoro(alcoxy vinyl ether), trifluoro ethylene, perfluoro alkyl ethylene, vinylidene fluoride, and ethylene. Modified PTFE generally has a viscosity of 10^{10} poise. A porous layer of non-melt-processable resin is created from an original material in the following manner.

[0052] The original material is made into fibers by sintering, which are then formed into a porous film;

[0053] The original material is made into an unsintered film by paste extrusion, which is then biaxially drawn and formed into a porous film (if the material is PTFE, the porous PTFE film produced in this manner is called expanded PTFE);

[0054] The original material in the form of an unsintered film is formed into a porous film by slitting/drawing the unsintered film;

[0055] The original material in the form of an unsintered film is sintered or semi-sintered, uniaxially drawn and defibrillated with machine abrasion to be formed into a porous film;

[0056] The original material is made into an unsintered film. The unsintered film is then baked or semi-baked, uniaxially drawn and split using a water jet needle process to be formed into a porous film;

[0057] When PTFE or modified PTFE is used, particles of PTFE or modified PTFE are partially fused to be formed into a porous film layer; and

[0058] PTFE resin coating is applied to the glass fiber layer until a porous layer of PTFE is formed.

[0059] <u>Melt-processable resin:</u>

[0060] Examples of melt-processable resin include tetrafluoroethylene-perfluoro (alkyl vinyl ether) copolymer (PFA), tetrafluoro ethylene-hexafluoro propene copolymer (FEP), polychloro trifluoro ethylene (PCTFE), tetrafluoro ethylene-ethylene copolymer (ETFE), tetrafluoro ethylene-hexafluoro propene-ethylene copolymer (EFEP), tetrafluoro ethylene-vinylidene fluoride copolymer (PVdF). A porous layer of melt-processable resin is created from an original material in the following manner.

[0061] The original material is made into fibers by melt-extrusion, which are then formed into a porous film;

[0062] The original material in the form of an extruded film is formed into a porous film by slitting/drawing; and

[0063] The original material in the form of an extruded film is uniaxially drawn and defibrillated into a porous film.

[0064] <PTFE porous fiber>

[0065] Preferably, the porous fluoropolymer layer 33 is made of PTFE porous fiber. PTFE porous fiber is preferable because of its high oxygen content, and also its high

viscosity at the fusing point. Figure 3 shows an example of a fire-retardant composite material using a non-woven fabric film made of a PTFE fiber.

[0066] Generally, when the matrix resin content in the fire retardant layer increases, the ability to retard the spread of a fire is compromised. This is also the case with PTFE-based materials. Therefore, it is desirable to increase the apparent density of the PTFE-based material. Preferably, the fluoropolymer layer should have the apparent density of 0.2 to 1.5 g/cm^3. For example, a non-woven fabric film made of machine-abraded PTFE fibers with microporous diameter was formed to have the apparent density of 0.5 to 1.2 g/cm^3, which is more preferable. Such fluoropolymer layer should have the mean CP porous diameter of at least 0.5 μm. When a film of fibers is made with a mean diameter of about 13 μm (measurement was conducted using optical diameter of fiber analyzer (ODDA 100), a measurement system of Japan Wool Products Inspection Institute Foundation) the porous film had excellent drapeability, which makes the porous film particularly suitable for bonding to three-dimensional curved surfaces. Furthermore, when this porous film was made more dense using a calendar roll to have the apparent density at 1 g/cm^3, a film of porous fiber with the mean CP porous diameter of 4.5 μm (measurement was performed with Coulter porometer manufactured by Beckman) was obtained. The porous material with such diameter had excellent workability and impregnation as compared with the PTFE-drawn porous membrane having porous diameter of 0.5 to 1 μm.

[0067] Here, the porous fluoropolymer layer 33 and or one of the structural layers 31A and 31B may have one of hydroxide, salt, and oxide of an alkali-earth metal mixed therein, such that the alkali earth metal is disposed in the porous fluoropolymer layer or in close proximity thereto. This way, fluoride that is generated at time of pyrolysis of the PTFE layer can be neutralized. For instance, calcium may be pre-mixed with the porous fluoropolymer layer in order to induce a reaction to neutralize hydrofluoric acid, thereby yielding calcium fluoride and preventing generation of hydrogen fluoride, which is a toxic gas, at the time of fire.

[0068] In the example discussed above, the fire-retardant composite material uses a non-woven fabric of PTFE as the porous fluoropolymer layer. The non-woven fabric is made by subjecting a PTFE raw tape to semi-sintering or sintering treatment, drawing the sintered or semi-sintered tape uniaxially, and then defibrillating the tape by abrasion. This non-woven fabric has excellent base-resin impregnability and drapeability. Therefore, it

can be used as the fire-retardant layer in a composite material that is to be formed into a three-dimensional shape. Furthermore, even when the composite material is deformed by press-molding after impregnation, the fire-retardant layer is not damaged since it readily deforms by stretching.

[0069] <Molding>

[0070] To mold the composite material shown in Figure 3, the following two methods are commonly used. In the methods described below, a porous film of PTFE fiber is used to create the porous fluoropolymer layer.

[0071] (1) Bonding/Laminating method (open system)

[0072] Gel coat is applied to a surface of a mold, such that a gel coat layer 35 is formed on the surface. Then, a film of a PTFE fiber layer 33 is placed onto the gel coat layer 35. After matrix resin is applied onto the PTFE fiber layer 33, a sheet of glass veil 36 and a sheet of intumescent mineral wool 37 are placed on the PTFE fiber layer 33, either separately or after being combined into one sheet. After the matrix resin is applied onto the intumescent layer 37, a sheet of glass fiber 31B is placed onto the intumescent layer 37. Then, a balsa member 32 and a sheet of glass fiber 31A are placed onto the glass fiber layer 31B in this order. The balsa member 32 is pre-treated to be coated with a matrix resin, such that the sheets of glass fiber 31A and 31B can be attached thereto. Here, the matrix resin is applied by hand. However, the actual process of applying the matrix resin will vary by size, complexity of the complete composite part. It will be apparent to one ordinarily skilled in the art what type of process of applying the matrix resin is suitable in a given circumstance.

[0073] (2) Vacuum Laminating method (closed system)

[0074] Alternatively, the fire-retardant composite material of the present invention can be formed in a vacuum laminating method shown in Figure 4. In this method, impregnation of the matrix resin is accomplished herein by injecting the matrix resin into the mold. In the fire-retardant composite material of Figure 4, the glass veil layer36 and the intumescent layer 37 are omitted.

[0075] Gel coat is applied to a surface of a mold 40, such that a gel coat layer 35 is formed on its surface. Then, a film of a PTFE fiber is placed onto the gel coat layer 35 to form a porous PTFE fiber layer 33. A sheet of glass fiber 31B is then placed onto the PTFE fiber layer 33. The sheet of glass fiber 31B may be placed onto the PTFE fiber

layer 33 with the intumescent layer 37 therebetween. Alternatively, the glass veil layer 36 may further be interposed between the PTFE fiber layer 33 and the intumescent layer 37. When the sheet of glass fiber layer 31B is directly placed onto the PTFE fiber layer 33, the sheet of glass fiber layer 31B and the PTFE fiber film 33 may be combined into one layer in advance by entanglement. Then, a balsa member 32 and a sheet of glass fiber 31A are placed onto the glass fiber layer 31B in this order. Thereafter, a cover 41, which is made of non-air-permeable material to assure tight sealing, is wrapped over the glass fiber layer 31A. While a vacuum pump (not shown) exhausts the air through an air outlet nozzle 42 provided in between the cover 41 and the glass fiber layer 31A to keep the inner pressure lower than the atmospheric pressure, the matrix resin is injected through nozzle 36 to infuse the matrix resin. Since the matrix resin is injected under pressure, the entire areas of the glass fiber layers 31A and 31B and the PTFE fiber layer 33 can be filled with the matrix resin due to the pressure difference.

[0076] Although there is only one each of resin injection nozzle 43 and air outlet nozzle 42, for injection of the matrix resin in Figure 4, there may be a plurality of nozzles. It is apparent to one ordinarily skilled in the art that there may be nozzles for air exhaustions and matrix resin injection provided in between the mold 40 and the gel coat layer 35, since it would be difficult to impregnate the matrix resin on the glass fiber layer 31A without nozzles for matrix resin injection on the bottom side of the mold 40.

[0077] To prevent air pollution, the solvent for the matrix resin can be condensed and recovered after being pressurized with the vacuum pump and cooled. Alternatively, the solvent can be treated with active carbon and absorbed.

[0078] A fire-retardant composite material according to the present invention is made with a porous fluoropolymer, and is therefore superior in terms of preventing fires that start from an external source. Also, the porous fluoropolymer non woven fabric used to make these composites has adequate thickness for mechanical performance, and good drapeability necessary to make parts having three dimensional shapes. Furthermore, the porous fluoropolymer fire retardant layer does not rely upon expansion to slow the spread of a fire. Therefore, the porous fluoropolymer layer can be firmly held in place by the composite during exposure to fire.

[0079] As used herein, the following directional terms "forward, rearward, above, downward, vertical, horizontal, below and transverse" as well as any other similar

directional terms refer to those directions of a vehicle equipped with the present invention. Accordingly, these terms, as utilized to describe the present invention should be interpreted relative to a vehicle equipped with the present invention.

[0080] The term "configured" as used herein to describe a component, section or part of a device includes hardware and/or software that is constructed and/or programmed to carry out the desired function.

[0081] Moreover, terms that are expressed as "means-plus function" in the claims should include any structure that can be utilized to carry out the function of that part of the present invention.

[0082] The terms of degree such as "substantially," "about" and "approximately" as used herein mean a reasonable amount of deviation of the modified term such that the end result is not significantly changed. For example, these terms can be construed as including a deviation of at least ± 5% of the modified term if this deviation would not negate the meaning of the word it modifies.

[0083] While only selected embodiments have been chosen to illustrate the present invention, it will be apparent to those skilled in the art from this disclosure that various changes and modifications can be made herein without departing from the scope of the invention as defined in the appended claims. Furthermore, the foregoing descriptions of the embodiments according to the present invention are provided for illustration only, and not for the purpose of limiting the invention as defined by the appended claims and their equivalents. Thus, the scope of the invention is not limited to the disclosed embodiments.

WHAT IS CLAIMED IS:

1. A fire-retardant composite material comprising

a fire retardant layer having a porous fluoropolymer layer;

a structural layer; and

a matrix resin impregnated at least partially into said porous fluoropolymer layer and said structural layer such that said porous fluoropolymer layer and said structural layer are attached to one another.

2. The fire-retardant composite material according to claim 1, wherein said porous fluoropolymer layer is made of at least one selected from the group consisting of expanded PTFE, woven fabric, non-woven fabric, felt, fiber, and powder.

3. The fire-retardant composite material according to claim 1, wherein said porous fluoropolymer layer is made of non-melt-processable resin.

4. The fire-retardant composite material according to claim 3, wherein said porous fluoropolymer layer is made of PTFE .

5. The fire-retardant composite material according to claim 4 wherein said porous fluoropolymer layer is made of fibers of PTFE.

6. The fire-retardant composite material according to claim 3 wherein said porous fluoropolymer layer is made of modified PTFE.

7. The fire-retardant composite material according to claim 6, wherein said modified PTFE is created by copolymerizing PTFE with at least one selected from the group consisting of hexafluoro propene, chloro trifluoro ethylene, perfluoro(alkyl vinyl ether), perfluoro(alcoxy vinyl ether), trifluoro ethylene, perfluoro alkyl ethylene, vinylidene fluoride, and ethylene.

8. The fire-retardant composite material according to claim 1 wherein

said porous fluoropolymer layer has a mean CP porous diameter of at least 0.5 μm.

9. The fire-retardant composite material according to claim 8 wherein said porous fluoropolymer layer has a mean CP porous diameter of at least 4.5 μm.

10. The fire-retardant composite material according to claim 1 wherein said matrix resin is at least one selected from the group consisting of vinyl ester resin, vinyl ester bromide resin, epoxy resin, unsaturated polyester resin, epoxy acrylate resin, polyimide resin, phenolic, and bismaleimide resin.

11. The fire-retardant composite material according to claim 1 wherein said structural layer is made of at least one selected from the group consisting of glass fiber, carbon fiber, alumina fiber, silicon carbide fiber, boron fiber, p-Aramid fiber, polybenzimidazol fiber, poly-ether-ether keton, graphite, and poly-p-phenylbenz-bisthiazol fiber.

12. The fire-retardant composite material according to claim 1 wherein said structural layer includes first and second reinforcement layers and a core layer, said core layer being provided between said first and second reinforcement layers, such that one of said porous fluoropolymer layer and said core layer being provided at a surface of one of said first and second reinforcement layers, and the other of said porous fluoropolymer layer and said core layer being provided at a surface of the other of said first and second reinforcement layers.

13. The fire-retardant composite material according to claim 12 wherein said porous fluoropolymer layer is combined with one of said first and second reinforcement layers by entanglement in advance.

14. The fire-retardant composite material according to claim 12 wherein

said fire retardant layer further includes an intumescent layer that is interposed between said porous fluoropolymer layer and said structural layer.

15. The fire-retardant composite material according to claim 14 wherein said fire retardant layer further includes a holding layer that is interposed between said intumescent layer and said fluoropolymer layer to hold said intumescent layer to said structural layer.

16. The fire-retardant composite material according to claim 15 wherein said porous fluoropolymer layer is combined with said holding layer by entanglement or blending in advance.

17. The fire-retardant composite material according to claim 1, wherein at least one of said porous fluoropolymer layer and said structural layer has one of hydroxide, salt, and oxide of an alkali-earth metal mixed therein.

18. The fire-retardant composite material according to claim 1, further comprising

a surface coating layer applied over said fire retardant layer.

19. A method of manufacturing a fire-retardant composite material, comprising the steps of:

applying a surface coat to an inner surface of a mold to form a surface coat layer;

forming a porous fluoropolymer layer over the surface coat layer;

placing a sheet of structural layer onto the fluoropolymer layer;

placing a core member onto the structural layer;

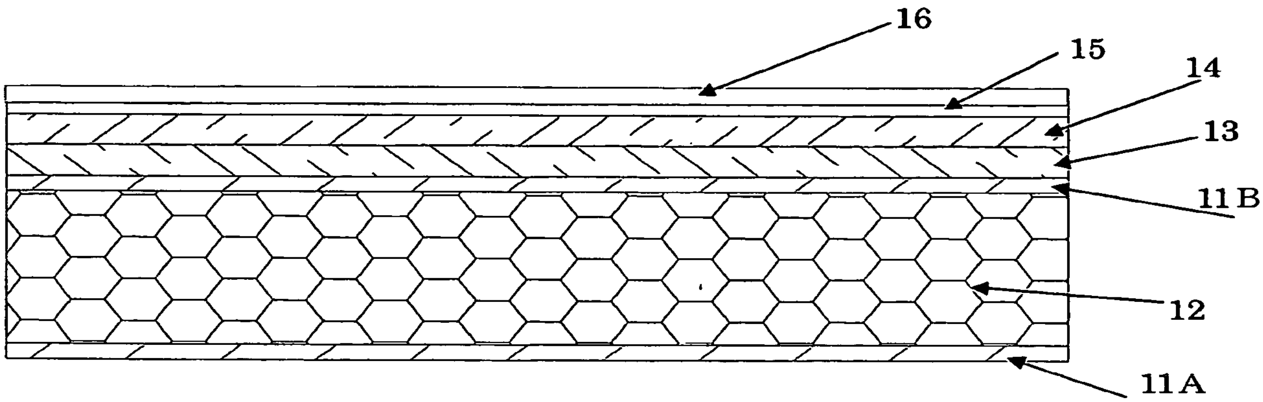
impregnating matrix resin at least partially into the core member and the structural layer, such that the structural layer is attached to the core member; and

impregnating matrix resin at least partially into the structural layer and the porous fluoropolymer layer, such that the porous fluoropolymer layer is attached to the structural layer.

A Fire-Retardant Composite Material

ABSTRACT OF THE DISCLOSURE

The fire-retardant composite material includes a balsa core member, glass fiber layers attached to either side of the core member, a PTFE fiber layer attached to one of the glass fiber layers, a gel coat provided over the PTFE fiber layer. Matrix resin bonds the glass fiber layer to the balsa core member, as well as the PTFE fiber layer to the glass fiber layer by impregnation.



PRIOR ART
Fig. 1

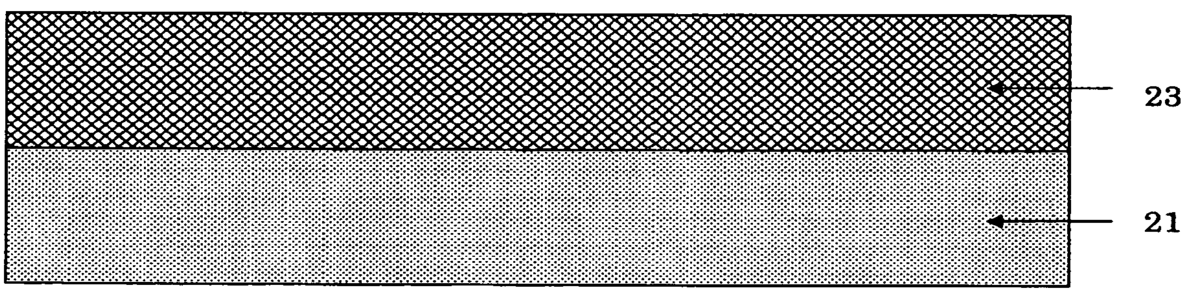


Fig. 2

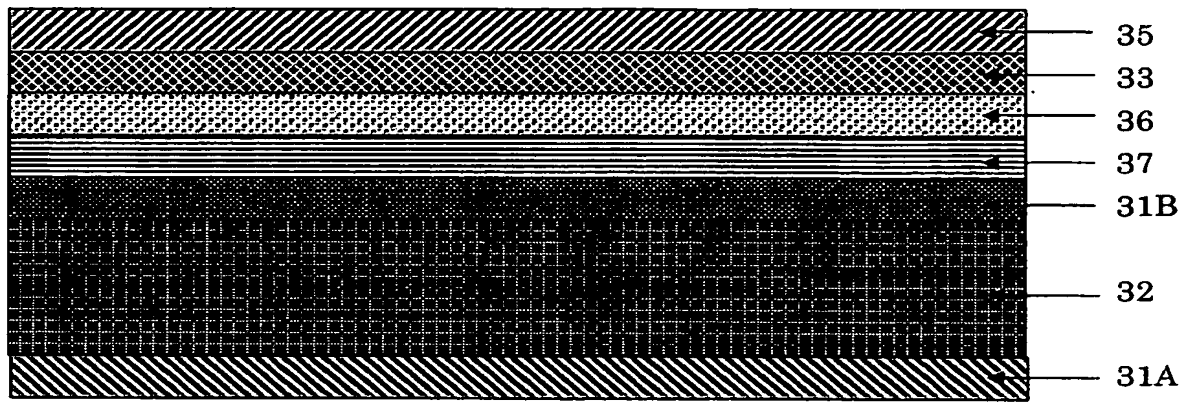


Fig. 3

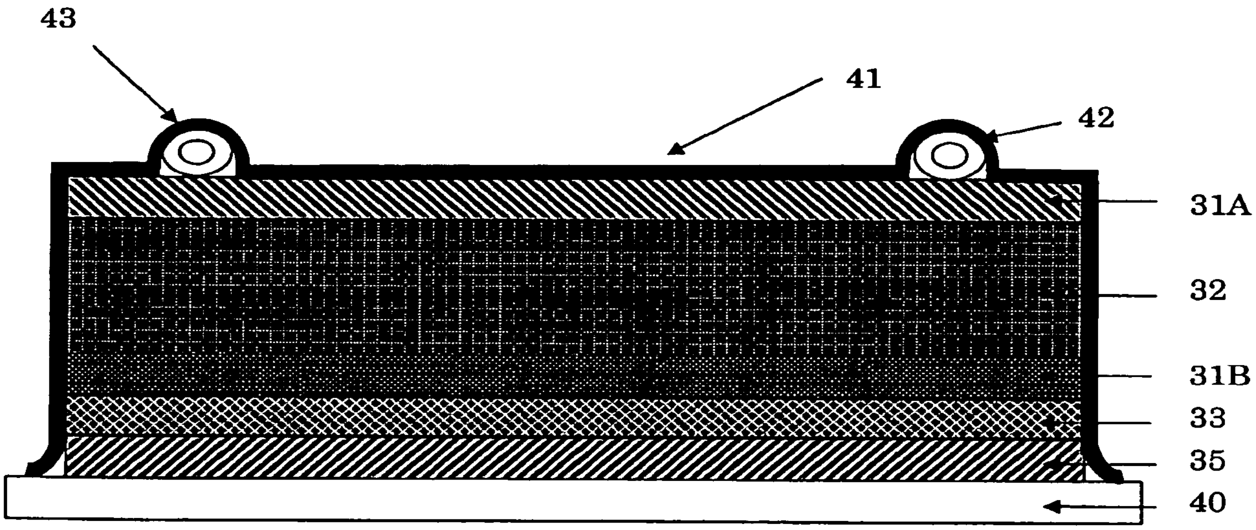


Fig. 4

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